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INDIANA UNIV AT BLOOMINGTON DEPT OF CHEMISTRY

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OXOTRIMOLYBDENUM (IV) ALKOXIDES: M03(MICRON 3-O)(MICRON 3-OR)(M-ETC(U)

MAY 81 M H CHISHOLM, K FOLTING, J C HUFFMAN

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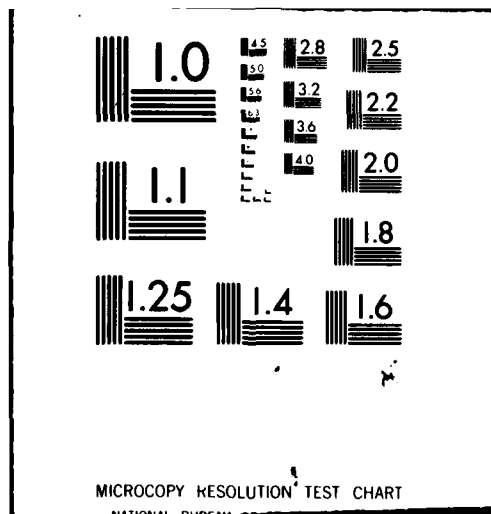
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OXOTRIMOLYBDENUM(IV) ALKOXIDES: $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu_2\text{-OR})_3(\text{OR})_6$,

WHERE R = i-Pr AND CH_2CMe_3 -

FROM SERENDIPITOUS DISCOVERY TO TOTAL SYNTHESIS.

by

10 M.H./Chisholm, K./Folting, J.C./Huffman and C.C./Kirkpatrick

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Mo TRIPLE BOND

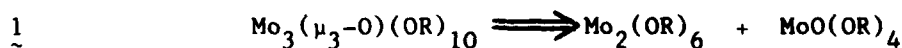
Oxotrimolybdenum(IV) Alkoxides: $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu_2\text{-OR})_3(\text{OR})_6$, where R = i-Pr and CH_2CMe_3 - From Serendipitous Discovery to Total Synthesis.

Sir:

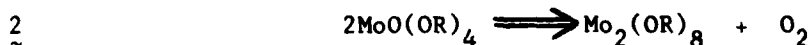
During the course of studies of the reactions between $\text{Mo}_2(\text{OR})_6$ compounds and molecular oxygen, which lead ultimately to $\text{MoO}_2(\text{OR})_2$ compounds with cleavage of the $\text{Mo}\equiv\text{Mo}$ bond,¹ we noted the formation of green intermediates when R = i-Pr and Ne (Ne = CH_2CMe_3). Indeed, from reactions involving $\text{Mo}_2(\text{ONe})_6$ and O_2 , we were able to isolate the green crystalline compound $\text{Mo}_3(\text{O})(\text{ONe})_{10}$, which was fully characterized by an X-ray study.² An ORTEP view of the central $\text{Mo}_3\text{O}(\text{OC})_{10}$ skeleton of the molecule is shown in Figure 1 along with some pertinent bond distances.

Since $\text{Mo}_3\text{O}(\text{ONe})_{10}$ is a member of a rapidly emerging class of triangulo molybdenum and tungsten containing compounds,^{3,4} we desired a general preparation of $\text{Mo}_3\text{O}(\text{OR})_{10}$ compounds.

A retrosynthetic analysis suggested that the triangulo $\text{Mo}_3(\mu_3\text{-O})$ unit could be constructed by the addition of an oxomolybdenum (6+) unit across the $\text{Mo}\equiv\text{Mo}$ bond as in 1. This bears analogy with the approach to cluster synthesis adopted by Stone and coworkers involving $\text{M}=\text{CR}_2$ and $\text{M}\equiv\text{CR}$ groups.⁵



The oxomolybdenum (6+) alkoxides, $\text{MoO}(\text{OR})_4$, which were unknown, were viewed as the products of a simple replacement of a $\text{Mo}\equiv\text{Mo}$ bond⁶ by two $\text{Mo}=\text{O}$ bonds in the oxygenolysis reaction 2. Previously it had been shown⁷ that the three electron ligand, NO, readily cleaves the $\text{Mo}\equiv\text{Mo}$ bond to give two $\text{Mo}-\text{NO}$ bonds, which may be formally viewed as $\text{M}\equiv\text{N}-\text{O}$.⁷



This synthetic strategy was successful in providing near quantitative yields of $\text{Mo}_3\text{O}(\text{OR})_{10}$ compounds, where R = Ne and i-Pr.⁸

Extensions of this approach to the synthesis of triangulo heterometallic species will be investigated.⁹

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References

1. Chisholm, M.H.; Folting, K.; Huffman, J.C.; Kirkpatrick, C.C.; Ratermann, A.L. J. Am. Chem. Soc. 1981, 103, 1305.
2. Crystal data, collected at -161°C , using MoK α radiation, gave the following: $a = 35.56(2)$, $b = 18.97(1)$, $c = 19.34(1)$ Å, space group Pbcn, $Z = 8$, $d_{\text{calcd}} = 1.295 \text{ g cm}^{-3}$. Of the 10379 reflections measured in the range $6^{\circ} \leq 2\theta \leq 40^{\circ}$, 6102 were unique. Only 55% of the unique data were observed using the criteria $F \geq 2.33\sigma(F)$. In retrospect, this was proven to be caused by loss of a solvent molecule (CH_2Cl_2) and disorder of one of the ONe ligands (O(5) in Fig. 1) and high thermal motions of all the neopentyl groups. The structure was readily solved by direct methods and Fourier techniques and refined by full matrix least squares. Only the largest 1500 reflections were used in the refinement. Molybdenum atoms were assigned anisotropic thermal parameters and all other atoms, isotropic parameters. Two peaks that occurred in a void in the crystal were assigned as chlorine atoms, whose occupancy refined to 0.33. The carbon of the CH_2Cl_2 molecule was not discernable. Final residuals are $R(F) = 0.0752$ and $R_w(F) = 0.0759$.
3. Muller, A.; Jostes, R.; Cotton, F.A. Angew. Chem. Int. Ed. Engl. 1980, 19, 875.
4. Bino, A.; Cotton, F.A.; Dori, Z. J. Am. Chem. Soc. 1981, 103, 243.
5. Ashworth, T.V.; Chetcuti, M.J.; Farrugia, L.J.; Howard, J.A.K.; Jeffrey, J.C.; Mills, R.; Pain, G.N.; Stone, F.G.A.; Woodward, P. in "Reactivity of Metal-Metal Bonds", ACS Symposium Series 1981, 155, Ch. 15, M.H. Chisholm, Ed.
6. Chisholm, M.H.; Cotton, F.A.; Extine, M.W.; Reichert, W.W. Inorg. Chem. 1978, 17, 2944.
7. Chisholm, M.H.; Cotton, F.A.; Extine, M.W.; Kelly, R.L. J. Am. Chem. Soc. 1978, 100, 3354.
8. Preparation of $\text{MoO}(\text{OPr}^i)_4$. $\text{Mo}_2(\text{OPr}^i)_8$ (ref. 6) (1.8 g) was dissolved in dry toluene (25 mL) in a 250-mL round-bottomed flask under a nitrogen atmosphere. The solution was frozen at -198°C (1. N_2) and the flask was evacuated and attached to a vacuum manifold. Dry molecular oxygen was

added and the solution was thawed and warmed to room temperature. The solution changed rapidly from blue to green to pale yellow and was stirred for 1 h at room temperature under 1 atm O_2 . The solvent was stripped, yielding a yellow viscous liquid $MoO(OPr^i)_4$. The compound was vacuum distilled ($53^\circ C$, 10^{-4} mm Hg). Elemental analysis found (calcd for $MoO(OPr^i)_4$): C, 41.11 (41.38); H, 7.90 (8.10); N, 0.10 (0.00). The 1H NMR spectrum recorded in toluene- d_8 at 220 MHz, $16^\circ C$, showed a septet at $\delta = 4.77$ and a doublet at $\delta = 1.34$ (δ in ppm rel. Me_4Si). The natural abundance ^{17}O NMR spectrum recorded at $30^\circ C$ in benzene showed a singlet at $\delta = 894$ ppm with a peak width at half height of 150 Hz (δ ^{17}O relative to external $H_2^{17}O$). The narrow peak width is consistent with a terminal MoO group in a monomeric compound. A cryoscopic molecular weight determination in benzene also indicated that $MoO(OPr^i)_4$ is at least mostly monomeric in solution: $M = 410$ (calculated $M = 348$ for the monomer).

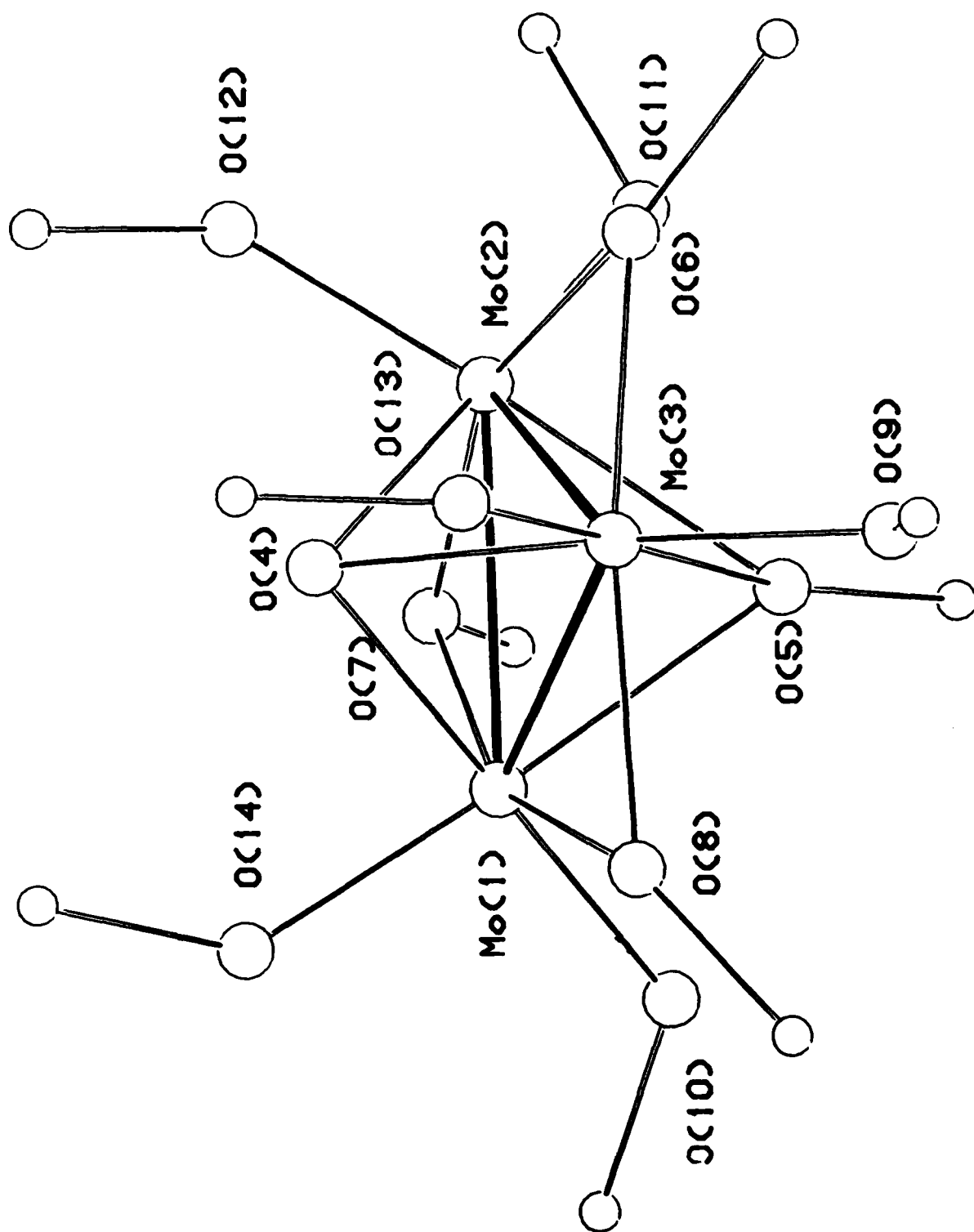
Preparation of $Mo_3O(OPr^i)_{10}$. $MoO(OPr^i)_4$ (1.84 mmol) was dissolved in dry degassed toluene (25 mL) in a 50-mL round-bottomed flask fitted with a side arm and magnetic spin bar under a nitrogen atmosphere. $Mo_2(OPr^i)_6$ (1 g, 1.84 mmol) was added via the side arm adaptor with stirring. The solution immediately turned from yellow to red and then to green. The solution was stirred for 1 h at room temperature and then the solvent was stripped and the green solids dissolved in CH_2Cl_2 (ca. 8 mL). The flask was placed in a refrigerator at ca. $-15^\circ C$ for 12 h, during which time green crystals, $Mo_3O(OPr^i)_{10}$, formed which were collected by filtration and dried in vacuo: yield 1.5 g (ca. 80% based on Mo). Elemental analyses found (calcd for $Mo_3O(OPr^i)_{10}$): C, 40.17 (40.27); H, 7.71 (7.89); N, 0.07 (0.00). The 1H NMR spectrum recorded in toluene- d_8 at 220 MHz, $16^\circ C$, showed septets at $\delta = 5.67$ (3H), 5.42 (3H), 4.64 (3H) and 4.00 (1H) and doublets at $\delta = 1.64$ (18H), 1.57 (18H), 1.19 (6H) and 1.16 (18H) with $J_{HH} = 7.0$ Hz. δ in ppm relative Me_4Si .

$MoO(ONe)_4$ and $Mo_3O(ONe)_{10}$, prepared in analogous reactions, are air-sensitive yellow and green crystalline solids, respectively. Both compounds gave satisfactory elemental analyses.

9. We thank the Office of Naval Research for support. MHC is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant and CCK is the 1980/81 Indiana University SOHIO Fellow.

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Caption to Figure 1. An ORTEP view of the central $\text{Mo}_3\text{O}(\text{OC})_{10}$ skeleton of the $\text{Mo}_3\text{O}(\text{ONe})_{10}$ molecule. All atoms are assigned arbitrary thermal parameters. Each molybdenum atom is in a distorted octahedral environment with respect to six directly bonded oxygen atoms. Pertinent bond distances in Angstroms (averaged) are Mo-to-Mo = 2.529(9) Å; Mo- $\mu_3\text{O}(\text{oxo})$ = 2.03(3); Mo- $\mu_3\text{OR}$ = 2.21(3); Mo- $\mu_2\text{OR}$ = 2.02(3); Mo-OR(terminal) trans to O(4) = 1.94(2); Mo-OR(terminal) trans to $\mu_3\text{-OR}$ = 1.85(3).



Abstract

Oxotrimolybdenum(IV) alkoxides, $\text{Mo}_3\text{O}(\text{OR})_{10}$ where R = isopropyl and neopentyl, have been discovered and are shown to be related to a rapidly emerging class of triangular early transition metal complexes recently reported by Cotton and coworkers. A high yield synthesis of the new compounds is described and involves the addition of an oxomolybdenum(6+) unit across a $\text{Mo}\equiv\text{Mo}$ bond.

Supplementary Crystallographic Data for

"Oxotrimolybdenum(IV) Alkoxides: $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu_2\text{-OR})_3(\text{OR})_6$,

where R = i-Pr and CH_2CMe_3 -

From Serendipitous Discovery to Total Synthesis."

Table 1: Fractional Coordinates and Isotropic Thermal Parameters for $\text{Mo}_3\text{O}(\text{OCH}_2\text{CMe}_3)_{10}$

Atom	x	y	z	Biso
Mo(1)	5952(1)	2582(2)	153(2)	22
Mo(2)	6247(1)	2604(2)	-1033(2)	20
Mo(3)	6373(1)	1580(2)	-220(2)	22
O(4)	6509(7)	2609(15)	-95(12)	27(6)
O(5)	5807(9)	1849(16)	-654(17)	36(9)
O(6)	6496(7)	1667(14)	-1240(12)	13(6)
O(7)	5876(8)	3261(14)	-643(14)	18(7)
O(8)	6048(9)	1659(16)	646(14)	31(7)
O(9)	6264(8)	568(14)	-271(13)	24(6)
O(10)	5425(7)	2551(16)	390(12)	27(6)
O(11)	6007(7)	2602(17)	-1930(11)	24(6)
O(12)	6626(9)	3233(17)	-1293(16)	38(8)
O(13)	6845(9)	1387(15)	144(16)	36(8)
O(14)	6086(9)	3239(16)	810(14)	27(7)
C(15)*	5411(26)	1809(46)	-997(47)	25(21)
C(16)*	5320(47)	1059(87)	-298(90)	100(52)
C(17)	5341(15)	1101(30)	-1161(28)	44(13)
C(18)	5563(18)	764(33)	-1680(31)	66(17)
C(19)*	5233(27)	679(50)	-429(43)	17(22)
C(20)*	4872(27)	993(55)	-1500(47)	31(23)
C(21)*	4999(32)	618(55)	-1124(57)	45(26)
C(22)*	5059(31)	1884(55)	-1502(52)	45(27)
C(23)	6539(13)	1199(24)	-1855(22)	26(11)
C(24)	6963(16)	1230(29)	-2148(26)	41(13)
C(25)	7007(15)	1937(27)	-2497(26)	41(13)
C(26)	7245(14)	1143(27)	-1531(23)	30(11)
C(27)	7022(19)	582(37)	-2636(34)	80(19)
C(28)	5519(14)	3551(27)	-909(26)	41(13)
C(29)	5520(16)	4386(29)	-877(28)	49(14)
C(30)	5842(15)	4659(28)	-1261(27)	46(14)
C(31)	5144(14)	4631(26)	-1239(24)	37(13)
C(32)	5508(12)	4613(22)	-128(23)	29(10)
C(33)	5839(11)	1154(21)	1105(21)	16(9)
C(34)	5982(15)	1167(28)	1867(24)	38(12)
C(35)	5755(17)	561(31)	2190(29)	58(15)
C(36)	5876(13)	1891(23)	2199(22)	23(10)
C(37)	6408(17)	1057(28)	1865(25)	50(13)
C(38)	6496(11)	0(23)	-10(20)	18(10)
C(39)	6314(12)	-693(21)	-140(21)	24(9)
C(40)	6303(11)	-862(19)	-927(18)	13(8)
C(41)	5902(13)	-734(24)	129(25)	38(11)
C(42)	6595(11)	-1283(18)	216(21)	12(8)
C(43)	5223(13)	2982(23)	916(22)	27(11)
C(44)	4811(13)	2732(25)	1011(23)	33(11)
C(45)	4637(15)	3134(28)	1581(26)	44(14)
C(46)	4783(13)	1926(23)	1167(24)	28(12)
C(47)	4640(13)	2808(25)	276(26)	41(12)
C(48)	6122(12)	3062(21)	-2504(21)	19(10)

Atom	x	y	z	Bi so
C(49)	5884(13)	2986(23)	-3127(22)	21(10)
C(50)	5956(14)	2280(28)	-3423(23)	41(12)
C(51)	5456(16)	3080(28)	-2963(27)	49(14)
C(52)	6046(20)	3489(40)	-3683(34)	93(20)
C(53)	6973(13)	3435(26)	-953(24)	34(11)
C(54)	7183(16)	4083(29)	-1247(27)	47(14)
C(55)	6884(15)	4728(28)	-1282(27)	49(14)
C(56)	7514(16)	4153(27)	-814(24)	45(12)
C(57)	7263(16)	3813(31)	-2066(27)	54(15)
C(58)	7125(15)	1852(25)	353(25)	35(12)
C(59)	7450(15)	1440(26)	662(23)	37(12)
C(60)	7763(21)	1983(37)	932(40)	106(23)
C(61)	7374(16)	834(31)	1221(31)	69(17)
C(62)	7672(19)	1160(35)	57(32)	80(18)
C(63)	6444(17)	3511(30)	986(28)	60(14)
C(64)	6457(18)	4139(29)	1582(27)	49(14)
C(65)	6865(26)	4247(48)	1875(44)	125(29)
C(66)	6076(22)	4419(42)	1729(38)	102(23)
C(67)	6260(30)	3698(60)	2380(54)	176(38)
Cl(68)	3606(12)	3455(22)	495(18)	125(18)
Cl(69)	3207(14)	2726(27)	1479(24)	82(20)

Notes:

- 1) Fractional coordinates are $\times 10^{**4}$ for non-hydrogen atoms and $\times 10^{**3}$ for hydrogen atoms. Biso values are $\times 10$.
- 2) Isotropic values for those atoms refined anisotropically are calculated using the formula given by W. C. Hamilton, Acta Cryst., 12,609 (1959)
- 3) Atoms marked by an asterisk (*) were disordered.
- 4) The occupancy factor for the Cl-atoms refined to an average value of 0.33.

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